Foundations of

Materials Science and Engineering

Lecture Note 10

June 10, 2013

Kwang Kim

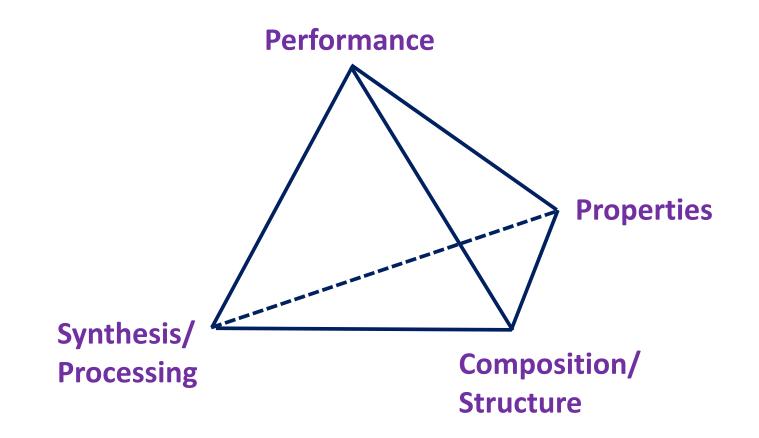
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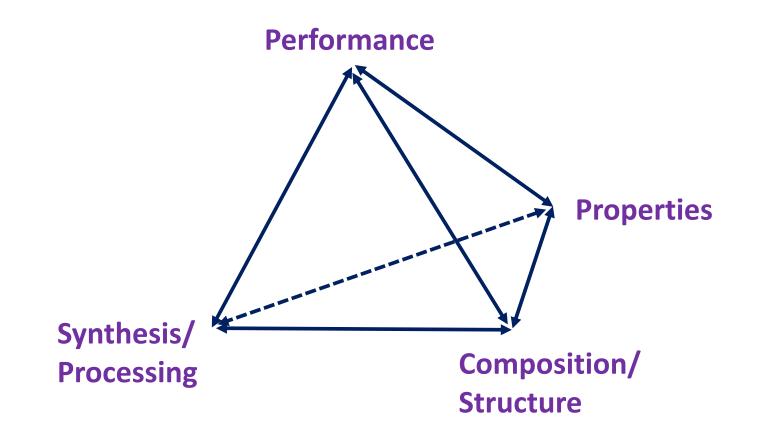
Material Science and Engineering (MSE)

"Tetrahedron of Materials Science and Engineering"

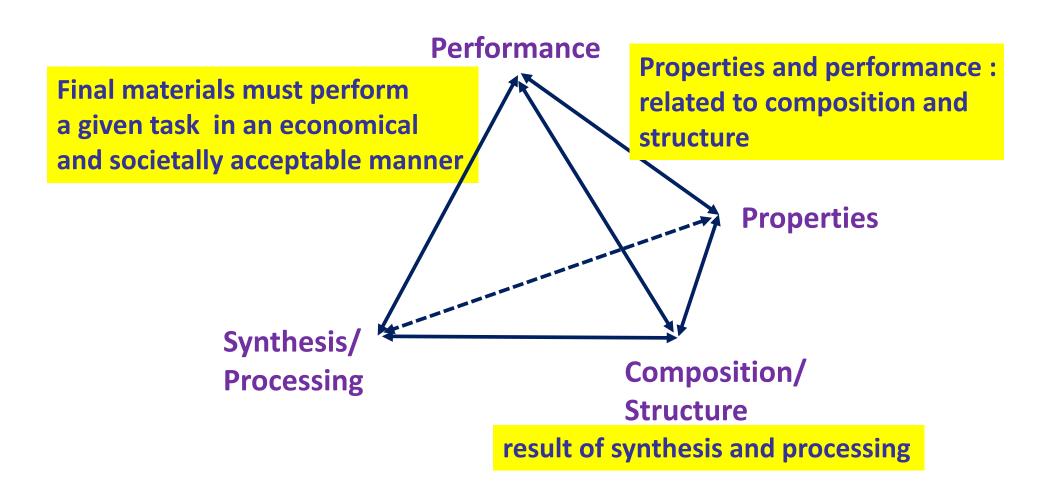


Material Science and Engineering (MSE)

Four elements of materials and strong interrelationship among them define a field of Materials Science and Engineering. Materials Science and Engineering rooted in the classical description of physics and chemistry



Material Science and Engineering (MSE)



1. Pick Application and Determine required Properties Properties: mechanical, electrical, thermal, magnetic, optical

2. Properties : Identify candidate Material(s) Material: structure, composition

3. Material : Identify required Processing

Processing: changes structure and overall shape ex: casting, sintering, vapor deposition, forming, joining,

Periodic Table

90

Th

**Actinides

7

91

Pa

7s²6d² 7s²5f²6d¹ 7s²5f³6d¹

92

U

93

Np

7s²5f⁴6d¹

95

Am

7s²5f⁷

94

Pu

 $7s^{2}5f^{6}$

96

Cm

7s25f76d1

97

Bk

 $7s^{2}5f^{9}$

98

Cf

99

Es

100

Fm

7s²5f¹⁰ 7s²5f¹¹ 7s²5f¹² 7s²5f¹³ 7s²5f¹⁴ 7s²5f¹⁴6d¹

101

Md

102

No

103

Lr

Atomic number increases Atomic radius increases Ionization energy decreases

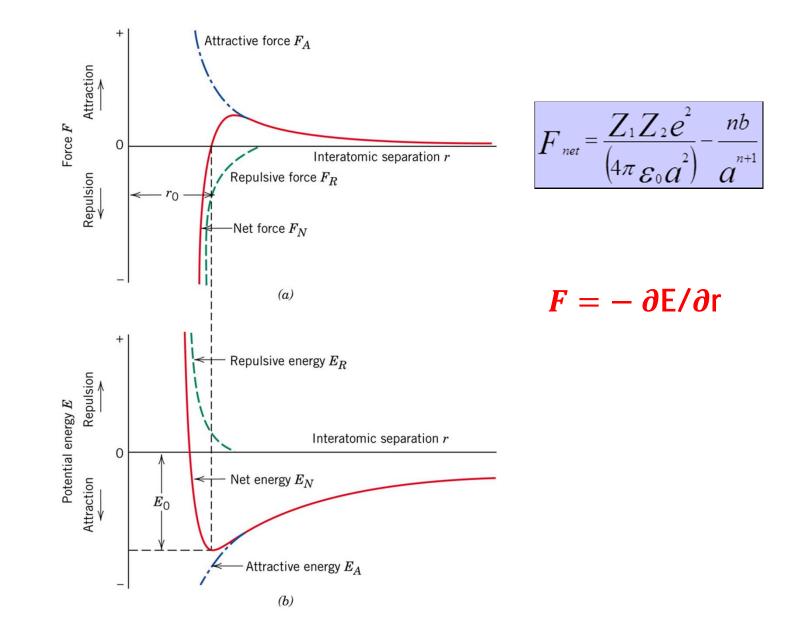
		Main-Group Elements (s block)								Main-Group Elements (<i>p</i> block)										
		1A (1) <i>ns</i> ¹		Atc	Atom <u>ic number increases</u> Atomic radius decreases Ionization energy increases															
	1	1 H 1s ¹	2A (2) ns ²	lon											4A (14) ns ² np ²	7A (17) ns ² np ⁵	2 He 1s ²			
le		3	4									ns ² np ¹ 5	6	ns ² np ³ 7	ns ² np ⁴	9	10			
rgy lev	2	Li 2 <i>s</i> ¹	Be 2s ²		Transition Elements (<i>d</i> block)									В 2s ² 2p ¹	C 2s ² 2p ²	N 2s ² 2p ³	O 2s ² 2p ⁴	F 2s ² 2p ⁵	Ne 2s ² 2p ⁶	
pied ener	3	11 Na 3s ¹	12 Mg 3s ²	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	(8)	— 8B — (9)	(10)	1B (11)	2B (12)	13 Al 3s ² 3p ¹	14 Si 3s ² 3p ²	15 P _{3s²3p³}	16 S 3s ² 3p ⁴	17 CI 3s ² 3p ⁵	18 Ar 3s ² 3p ⁶	
Period number: highest occupied energy level	4	19 K 4s ¹	20 Ca 4s ²	21 Sc 4s ² 3d ¹	22 Ti 4s ² 3d ²	23 V 4s ² 3d ³	24 Cr 4s ¹ 3d ⁵	25 Mn 4s ² 3d ⁵	26 Fe 4s ² 3d ⁶	27 Co 4s ² 3d ⁷	28 Ni 4s ² 3d ⁸	29 Cu 4s ¹ 3d ¹⁰	30 Zn	31 Ga	32 Ge 4s ² 4p ²	33 As 4s ² 4p ³	34 Se 4s ² 4p ⁴	35 Br 4s ² 4p ⁵	36 Kr 4s ² 4p ⁶	
umber: hiç	5	37 Rb 5s ¹	38 Sr 5 <i>s</i> ²	39 Y 5s ² 4d ¹	40 Zr 5s ² 4d ²	41 Nb 5s ¹ 4d ⁴	42 Mo 5s ¹ 4d ⁵	43 Tc _{5s²4d⁵}	44 Ru 5s ¹ 4d ⁷	45 Rh 5s ¹ 4d ⁸	46 Pd 4d ¹⁰	47 Ag 5s ¹ 4d ¹⁰	48 Cd 5s ² 4d ¹⁰	49 In 5s ² 5p ¹	50 Sn 5s ² 5p ²	51 Sb 5s ² 5p ³	52 Te 5s ² 5p ⁴	53 5s ² 5p ⁵	54 Xe _{5s²5p⁶}	
Period n	6	55 Cs _{6s} 1	56 Ba 6 <i>s</i> ²	57 La* 6s ² 5d ¹	72 Hf 6s ² 5d ²	73 Ta 6s ² 5d ³	74 W 6s ² 5d ⁴	75 Re 6s ² 5d ⁵	76 Os 6s ² 5d ⁶	77 Ir 6s ² 5d ⁷	78 Pt 6s ¹ 5d ⁹	79 Au 6s ¹ 5d ¹⁰	80 Hg 6s ² 5d ¹⁰	81 TI 6s ² 6p ¹	82 Pb 6s ² 6p ²	83 Bi 6s ² 6p ³	84 Po 6s ² 6p ⁴	85 At 6s ² 6p ⁵	86 Rn 6s ² 6p ⁶	
	7	87 Fr _{7s¹}	88 Ra 7 <i>s</i> ²	89 Ac** 7s ² 6d ¹	104 Rf 7 <i>s</i> ² 6 <i>d</i> ²	105 Db 7s ² 6d ³	106 Sg _{7s²6d⁴}	107 Bh 7s ² 6d ⁵	108 Hs _{7s²6d⁶}	109 Mt 7s ² 6d ⁷	110 Ds 7s ² 6d ⁸	111 Rg 7s ² 6d ⁹	112 _{7s²6d¹⁰}	113 7s ² 7p ¹	114 7s ² 7p ²	115 _{7s²7p³}	116 7s ² 7p ⁴			
	Inner Transition Elements (<i>f</i> block)																			
	6 *Lanthanides		anides	58 Ce _{6s²4f¹5d¹}	59 Pr _{6s²4f³}	60 Nd 6s ² 4f ⁴	61 Pm 6s ² 4f ⁵	62 Sm 6s ² 4f ⁶	63 Eu _{6s²4f⁷}	64 Gd _{6s²4f⁷5d¹}	65 Tb 6s ² 4f ⁹	66 Dy 6s ² 4f ¹⁰	67 Ho 6s ² 4f ¹¹	68 Er 6s ² 4f ¹²	69 Tm 6s ² 4f ¹³	70 Yb 6s ² 4f ¹⁴	71 Lu 6s ² 4f ¹⁴ 5d ¹			

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Primary Bonds

- Bonding with other atoms, the potential energy of each bonding atom is lowered resulting in a more stable state.
- Three primary bonding combinations : 1) metal-nonmetal, 2) nonmetal-nonmetal, and 3) metal-metal.
- **Ionic bonds** :- Strong atomic bonds due to transfer of **electrons**
- **Covalent bonds** :- Large interactive force due to sharing of **electrons**
- Metallic bonds :- Non-directional bonds formed by sharing of electrons
- **Permanent Dipole bonds** :- Weak intermolecular bonds due to attraction between the ends of permanent **dipoles**.
- Fluctuating Dipole bonds :- Very weak electric dipole bonds due to asymmetric distribution of electron densities.

Intermolecular Forces and Potentials



7 Crystal Systems

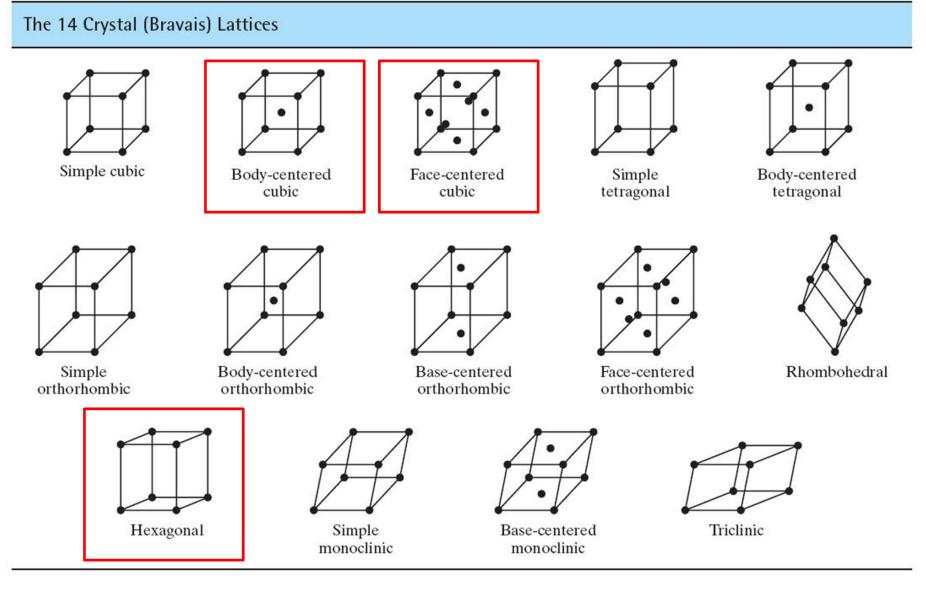
TABLE 3.1 The Seven Crystal Systems Unit cell geometry System Axial lengths and angles^a Cubic $a = b = c, \alpha = \beta = \gamma = 90^{\circ}$ C Hexagonal $a = b \neq c, \alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$ Tetragonal $a = b \neq c, \alpha = \beta = \gamma = 90^{\circ}$ Monoclinic $a \neq b \neq c, \alpha = \gamma = 90^{\circ} \neq \beta$ Orthorhombic $a \neq b \neq c, \alpha = \beta = \nu = 90^{\circ}$ Triclinic $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^{\circ}$ Rhombohedral $a = b = c, \alpha = \beta = \gamma \neq 90^{\circ}$

The lattice parameters *a*, *b*, and *c* are unit cell edge lengths.

The lattice parameters α , β , and γ are angles between adjacent unit-cell axes, where α is the angle viewed along the *a* axis (i.e., the angle between the *b* and *c* axes). The inequality sign(\neq) means that equality is not required.

14 Bravais Lattices

TABLE 3.2



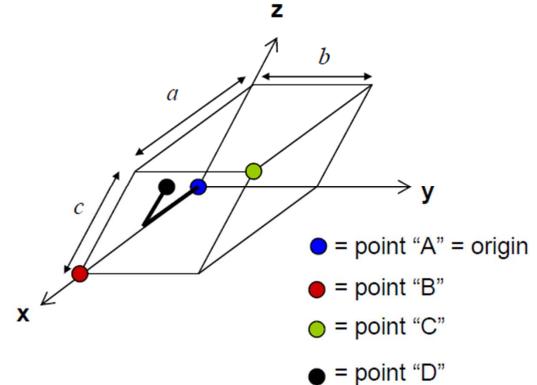
Atom Positions in Cubic Unit Cells

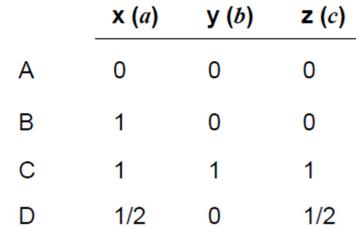
Point Coordinates

to define a point within a unit cell....

Essentially same as Cartesian coordinates except values of x, y, and z are expressed as fractions of the magnitude of unit vector(s) (and x, y, and z not necessarily orthogonal).

pt. coord.





Crystallographic Directions

To define a vector:

- 1. Start at the origin.
- Determine length of vector projection in each of 3 axes in units (or fractions) of *a*, *b*, and *c*.
- Multiply or divide by a common factor to reduce the lengths to the smallest integer values.

C

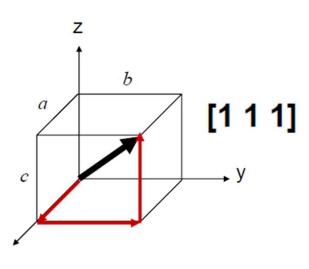
Х

Enclose in square brackets: [u v w] where u, v, and w are integers.

Along unit vectors: *a b*

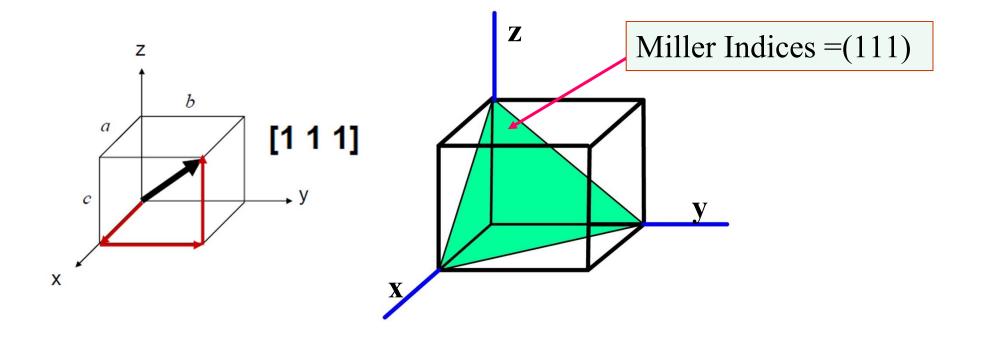
Note: in any of the 3 directions there are both directions.

Negative directions are denoted with a "bar" c



Miller Index

- Miller indices are used to specify directions and planes in lattices or in crystals.
- The number of indices will match with the dimension of the lattice or the crystal.

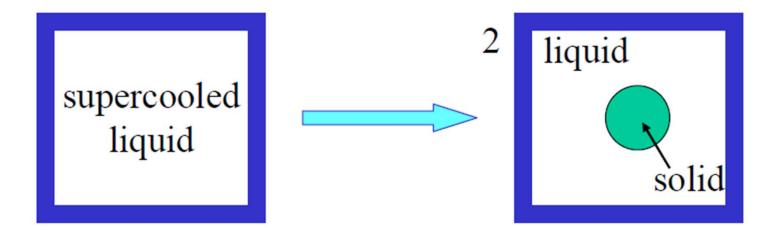


Solidification of Metals

Courtesy of Reynolds Metals Co.

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Energies Involved in Homogeneous Nucleation



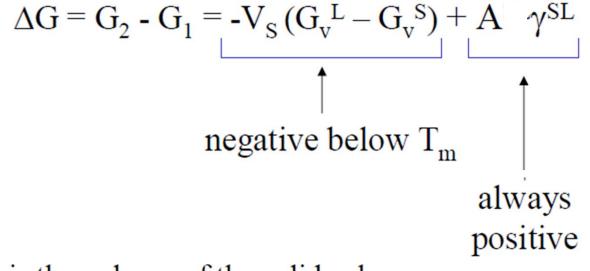
Is the transition from undercooled liquid to a solid spherical particle in the liquid a spontaneous one? That is, is the Gibbs free energy decreases?

The formation of a solid nucleus leads to a Gibbs free energy

change of ΔG

Energies Involved in Homogeneous Nucleation

The formation of a solid nucleus leads to a Gibbs free energy change of ΔG



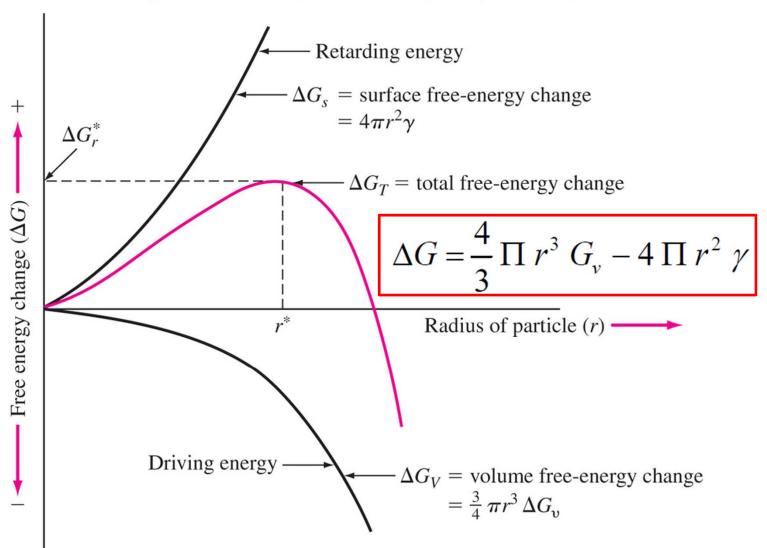
 V_s is the volume of the solid sphere

A^{SL} is the solid/liquid interfacial area

 γ^{SL} is the solid/liquid interfacial energy

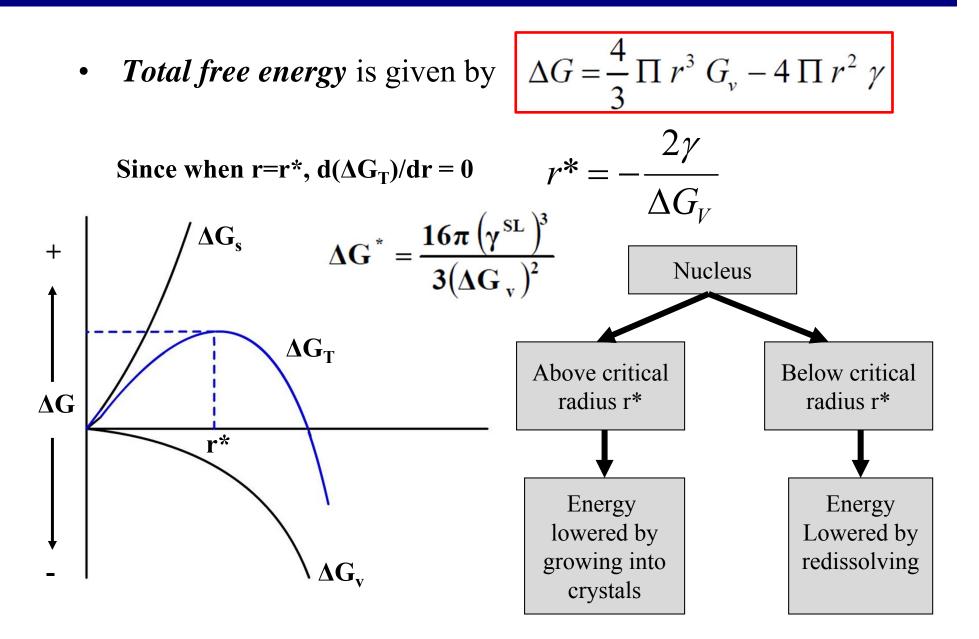
 $\Delta G_v = G_v^L - G_v^S$ is the volume free energy difference

Energies involved in homogenous nucleation



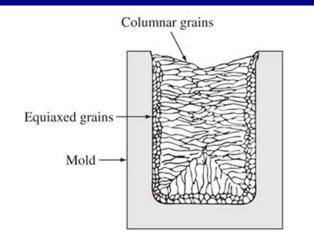
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Total Free Energy



Heterogeneous Nucleation





Heterogeneous nucleation occurs much more often than homogeneous nucleation. Heterogeneous nucleation applies to the phase transformation between any two phases of gas, liquid, or solid, typically for example, condensation of gas/vapor, solidification from liquid, bubble formation from liquid, etc.

Heterogeneous nucleation forms at preferential sites such as phase boundaries, surfaces (of container, bottles, etc.) or impurities like dust. At such preferential sites, the effective surface energy is lower, thus diminishes the free energy barrier and facilitating nucleation.

Defects in crystalline solids

1). Point Defect

- **①.** Impurity : In an alloy some unwanted elements may be existed.
- **2**. Vacancy : Missing atom from the lattice point.

2). Line Defect

Dislocation : Edge, screw and mixed dislocations

3). Planar Defect

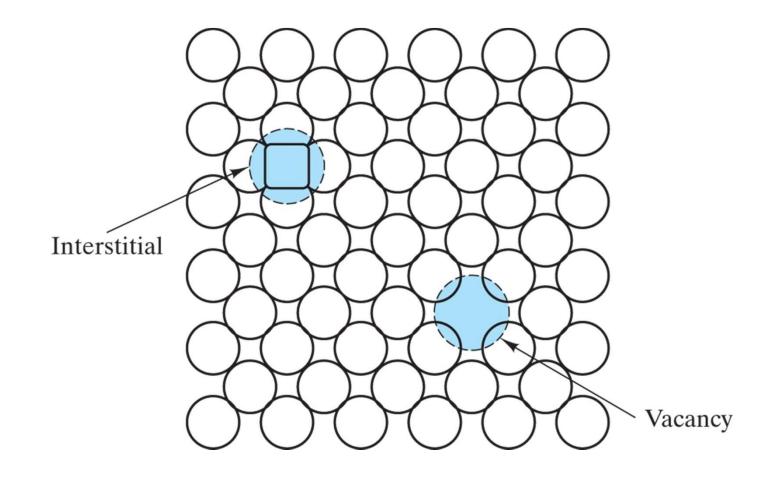
- **1**. Grain boundary
- **2**. Twin boundary
- **③**. Anti-phase domain boundary

4). Volumetric Defect

Void, Cracks, Shrinkage, inclusion, etc.

Point Defects

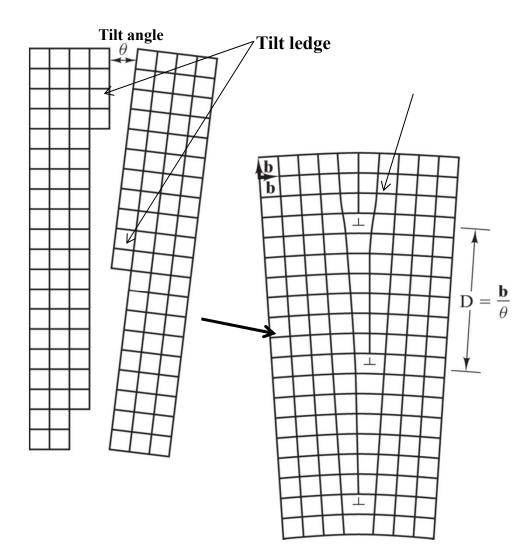
Two common point defects in metal or elemental semiconductor structures are the vacancy and the interstitial.



Edge Dislocation

- Created by insertion of extra half planes of atoms.
- ____ Positive edge dislocation
- Negative edge dislocation
- Burgers vector Shows displacement of atoms (slip).
 Edge displation of the edge displat

Grain Boundaries



This is termed a tilt boundary because it is formed when two adjacent crystalline grains are tilted relative to each other by a few degrees (θ). The resulting structure is equivalent to isolated edge dislocations separated by the distance b/ θ , where b is the length of the Burgers vector, b.

Elastic deformation: Metal returns to its original dimension after tensile force is removed.

Plastic deformation: Metal is deformed to such an extent such that it cannot return to its original dimension

Slip Mechanism

- During shear, atoms do not slide over each other.
- The slip occurs due to movement of dislocations.

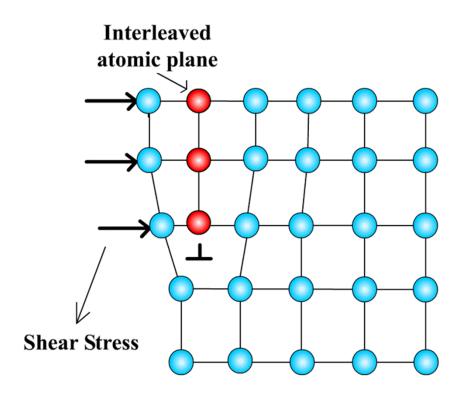
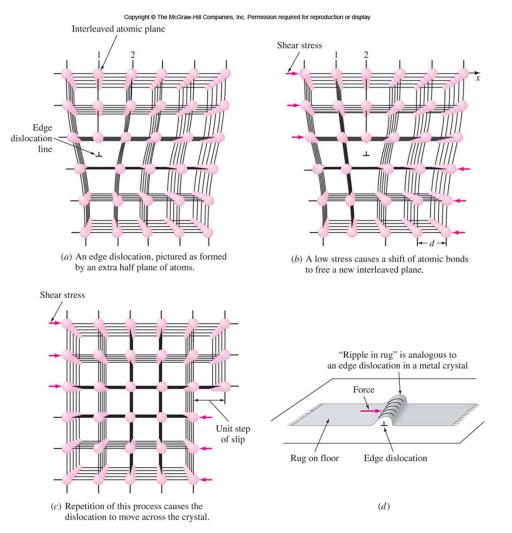


Figure 5.32

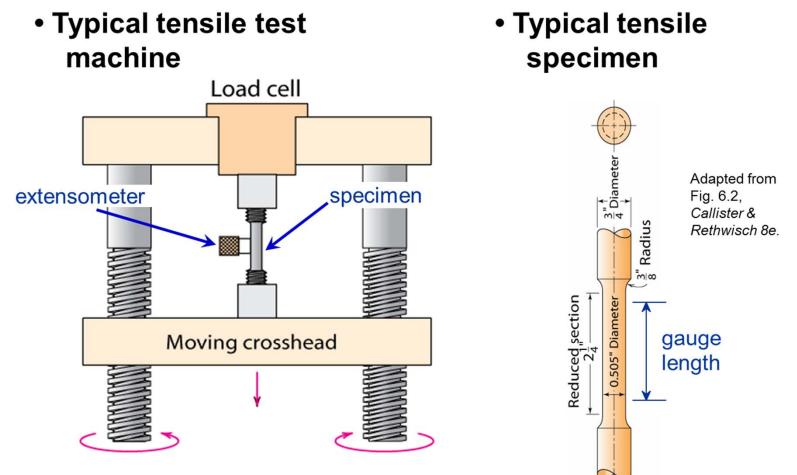
Slip Mechanism

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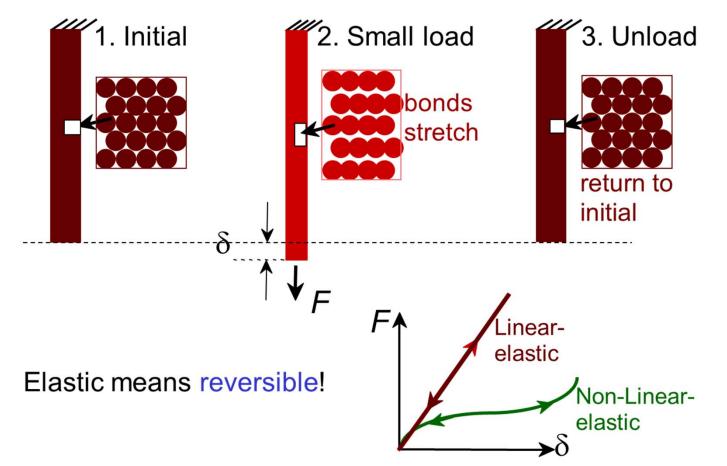
Tensile test

Stress-Strain Testing



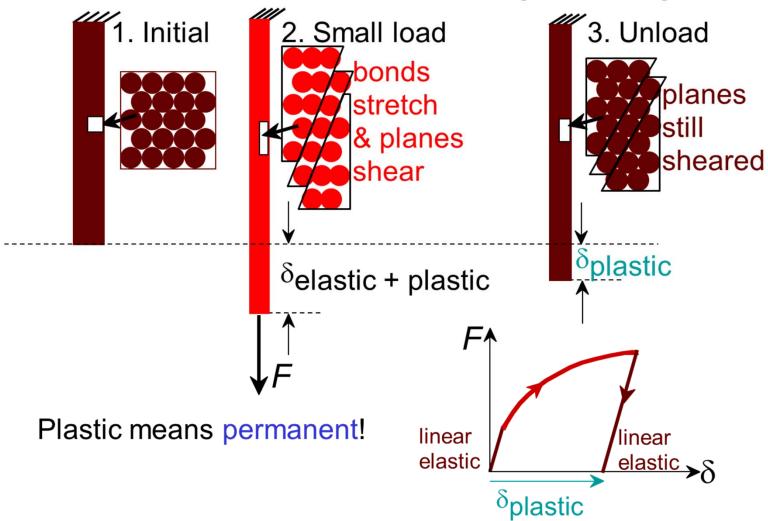
Adapted from Fig. 6.3, *Callister & Rethwisch 8e*. (Fig. 6.3 is taken from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, p. 2, John Wiley and Sons, New York, 1965.)

Elastic Deformation



Mechanical Properties

Plastic Deformation (Metals)



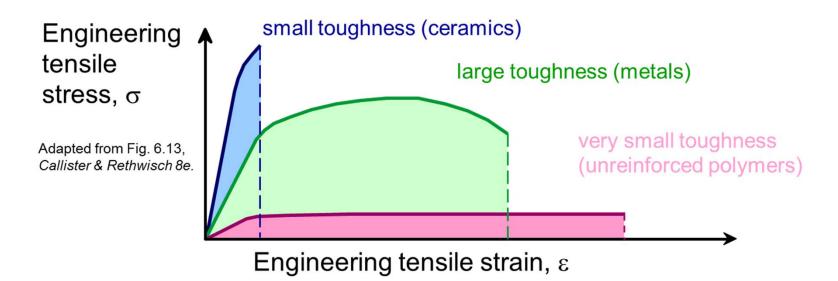
Mechanical Properties

Plastic (Permanent) Deformation (at lower temperatures, i.e. $T < T_{melt}/3$) • Simple tension test: Elastic+Plastic engineering stress, σ at larger stress Elastic initiall permanent (plastic) after load is removed $\rightarrow \epsilon_p \leftarrow$ engineering strain, $\boldsymbol{\epsilon}$ plastic strain Adapted from Fig. 6.10(a), Callister & Rethwisch 8e.



Toughness

- Energy to break a unit volume of material
- Approximate by the area under the stress-strain curve.



Brittle fracture: elastic energy Ductile fracture: elastic + plastic energy

Mixture of Ionic and Covalent Types. Depends on electronegativity difference.

Ceramic compound	Bonding atoms	Electronegativity difference	% ionic character	% covalent character
Zirconium dioxide, ZrO ₂	Zr–O	2.3	73	27
Magnesium oxide, MgO	Mg–O	2.2	69	31
Aluminum oxide, Al ₂ O ₃	Al–O	2.0	63	37
Silicon dioxide, SiO_2	Si–O	1.7	51	49
Silicon nitride, Si_3N_4	Si–N	1.3	34.5	65.5
Silicon carbide, SiC	Si–C	0.7	11	89

 Table 11.2
 Percent ionic and covalent bonding in some ceramic compounds

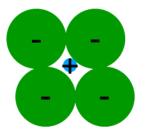
Ceramic Crystal Structures

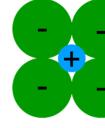
Oxide structures

- Oxygen anions (-ve ions) larger than metal cations (+ve ions)
- Close packed oxygen in a lattice (usually FCC)
- Cations fit into interstitial sites among oxygen ions

Factors that Determine Crystal Structure

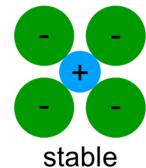
- 1. Relative sizes of ions Formation of stable structures:
 - --maximize the # of oppositely charged ion neighbors.



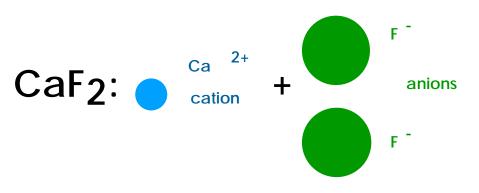


unstable

stable



Adapted from Fig. 12.1, *Callister & Rethwisch 8e.*



- 2. Maintenance of
 - Charge Neutrality :
 - --Net charge in ceramic
 - should be zero.
 - --Reflected in chemical
 - formula:

Simple Ionic Arrangements

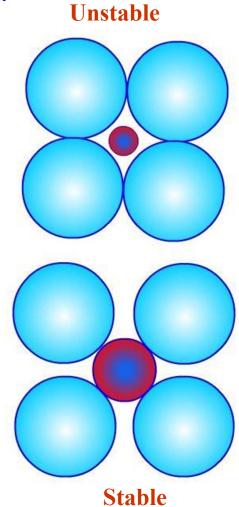
Packing of Ions depends upon Relative size of ions.

Need to balance electron charges.

If the anion does not touch the cation, then the arrangement is unstable.

Radius ratio = r_{cation}/r_{anion}

Critical radius ratio for stability for coordination numbers 8, 6 and 3 are > 0.732, > 0.414 and > 0.155, respectively.

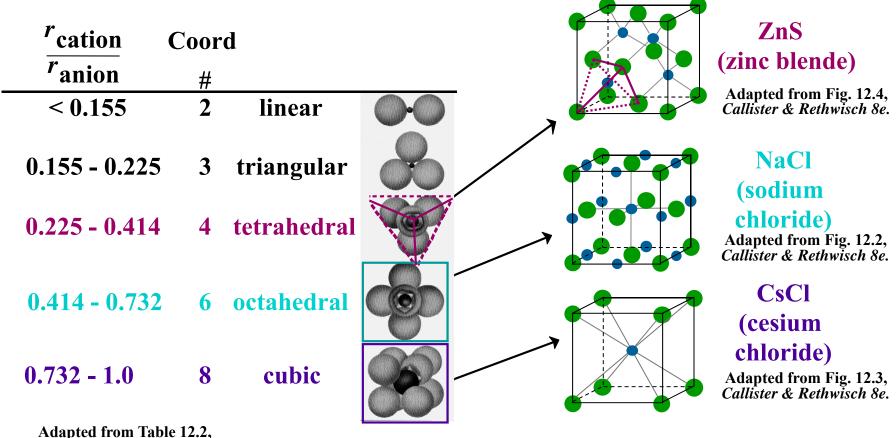


Coordination # and Ionic Radii

• Coordination # increases with

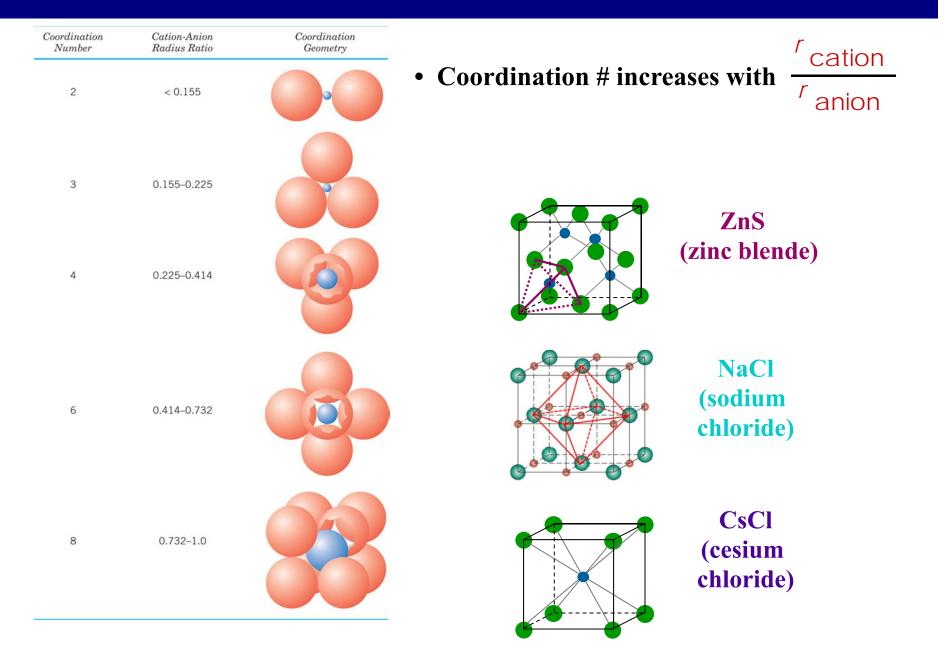
^r cation

To form a stable structure, how many anions can surround around a cation?

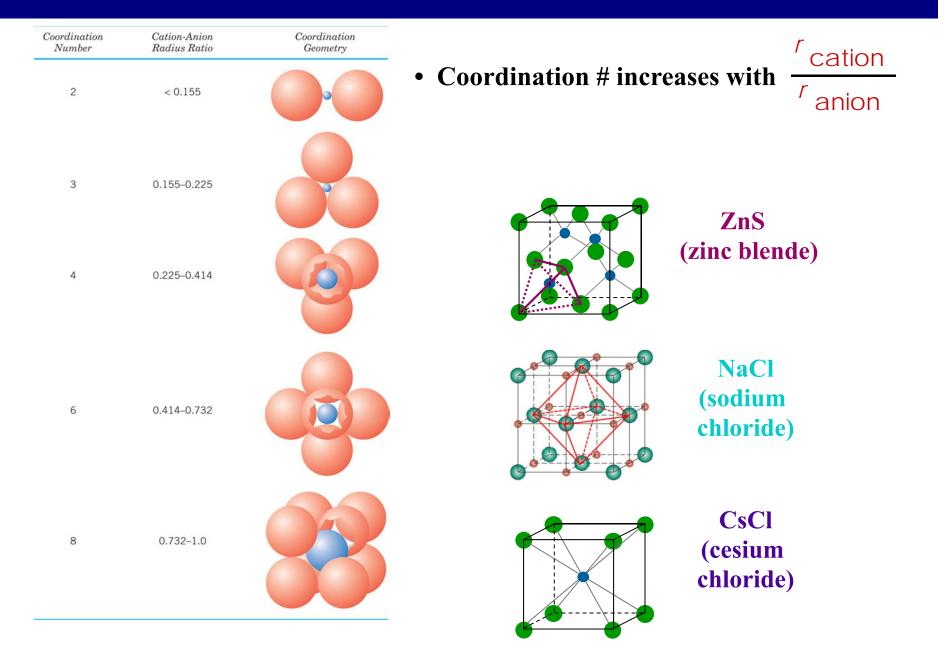


Callister & Rethwisch 8e.

Coordination # and Ionic Radii



Coordination # and Ionic Radii



Composites

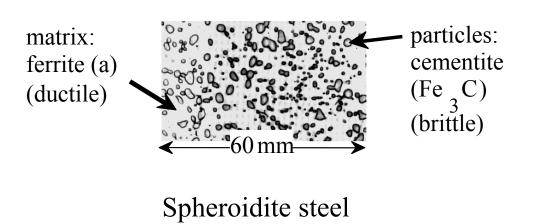
- Combination of two or more individual materials
- A composite material is a material system, a mixture or combination of two or more micro or macroconstituents that differ in form and composition and do not form a solution.
- Multiphase materials with chemically different phases and distinct interfaces
- Design goal: obtain a more desirable combination of properties (principle of combined action)

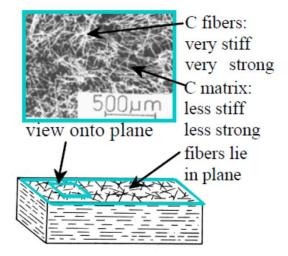
e.g., High-strength/light-weight, low cost, environmentally resistant

- Properties of composite materials can be superior to its individual components.
- Examples: Fiber reinforced plastics, concrete, asphalt, wood etc.

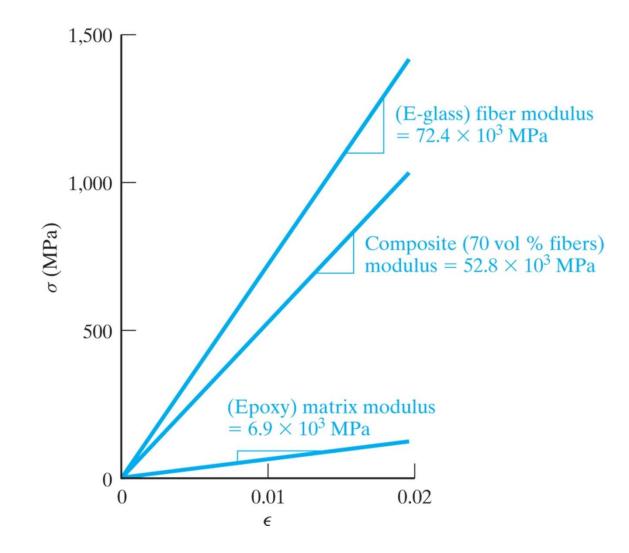
Composite Characteristics

- Matrix:
- softer, more flexible and continuous part that surrounds the other phase.
- transfer stress to other phases
- protect phases from environment
- Reinforcement (dispersed phase):
- stiffer, high strength part (particles or fibers are the most common).
- enhances matrix properties





Simple stress–strain plots for a composite and its fiber and matrix components. The slope of each plot gives the modulus of elasticity.



Composite

Depends on:

- properties of the matrix material.
- properties of reinforcement material.
- ratio of matrix to reinforcement.
- matrix-reinforcement bonding/adhesion.
- mode of fabrication.

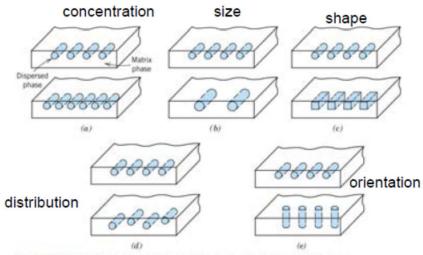
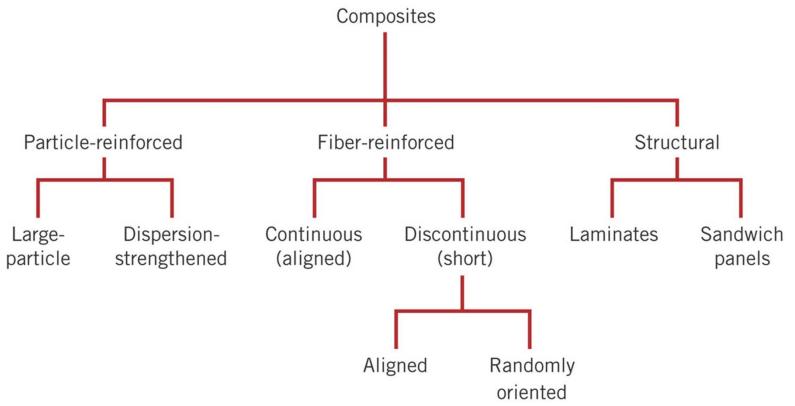


FIGURE 16.1 Schematic representations of the various geometrical and spatial characteristics of particles of the dispersed phase that may influence the properties of composites: (a) concentration, (b) size, (c) shape, (d) distribution, and (e) orientation. (From Richard A. Flinn and Paul K. Trojan, Engineering Materials and Their Applications, 4th edition. Copyright © 1990 by John Wiley & Sons, Inc. Adapted by permission of John Wiley & Sons, Inc.)

Reinforcement-based



Matrix of Composites

Fiber-Matrix Interface

1. Molecular entanglement (interdiffusion):

- Entanglement of molecules at the interface.
- Especially important in fibers that are precoated with polymers.
- Molecular conformation/structural and chemical aspects.

2. Electrostatic attraction

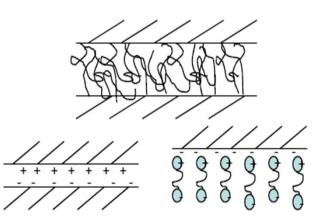
- Depends on surface charge density.
- e.g. glass fibers, polymers with chargeable groups.

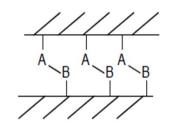
3. Covalent bonding

- Usually the strongest fiber matrix fiber-interaction.
- The most important in many composites.

4. Mechanical adhesion

- Interlocking of 2 rough surfaces
- e.g. thermosetting resins







Particle-Reinforced Composites

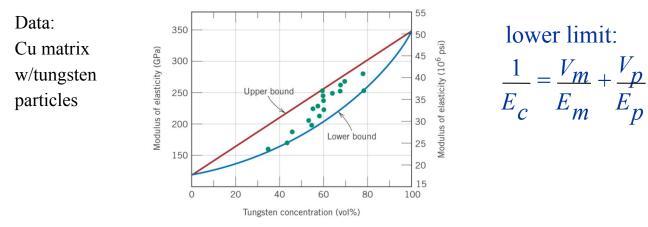
Particle-reinforced

Fiber-reinforced

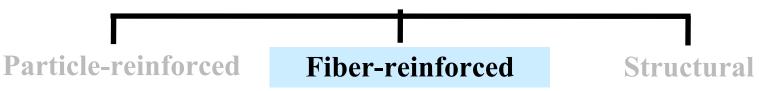
Structural

- Elastic modulus, *E_c*, of composites:
 - -- two "rule of mixture" extremes:

upper limit: $E_c = V_m E_m + V_p E_p$



- Application to other properties:
 - -- Electrical conductivity, σ_e : Replace *E*'s in equations with σ_e 's.
 - -- Thermal conductivity, k: Replace E's in equations with k's.



Fiber Phase

– Smaller diameter fiber is stronger than bulk in most materials

Whiskers

- very thin single crystals that have extremely large aspect ratios.
- high degree of crystallinity and virtually flaw free exceptionally high strength.
- usually extremely expensive.
- some whisker materials: graphite, SiC, silicon nitride, aluminum oxide.

Fibers

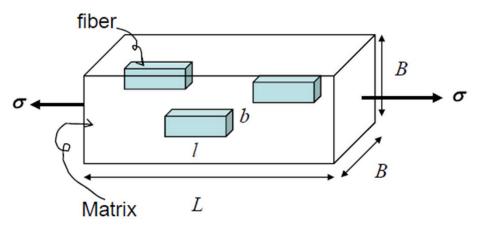
- polycrystalline or amorphous.
- typically: polymers or ceramics (polymer aramids, glass, carbon, boron, SiC...

Fine Wires

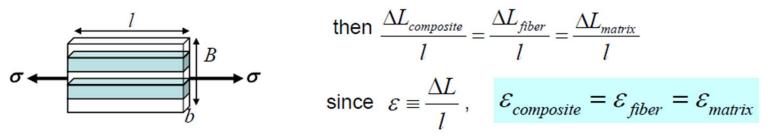
- relatively large diameter, often metal wires.
- e.g. steel, molybdenum,

Continuous-aligned fibers

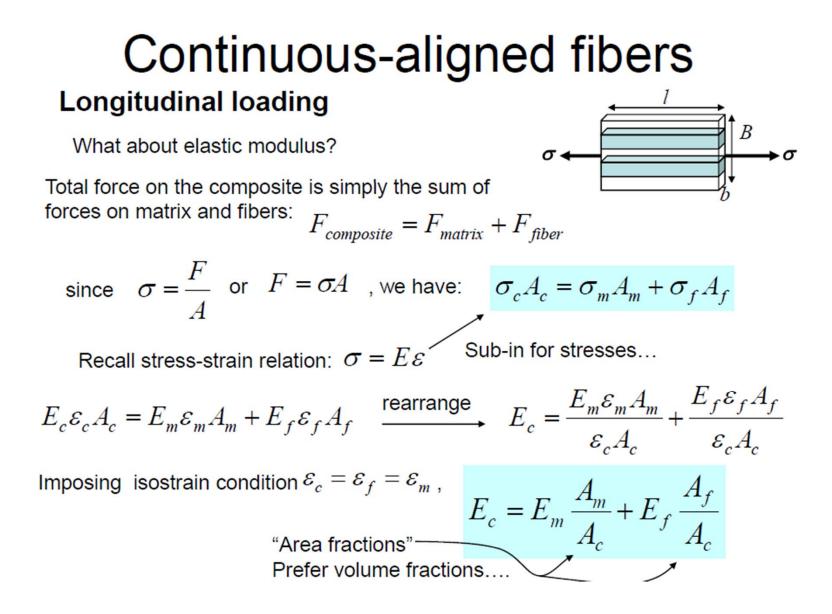
Consider a composite with fibers having square rod geometry with stress in the **longitudinal direction**...

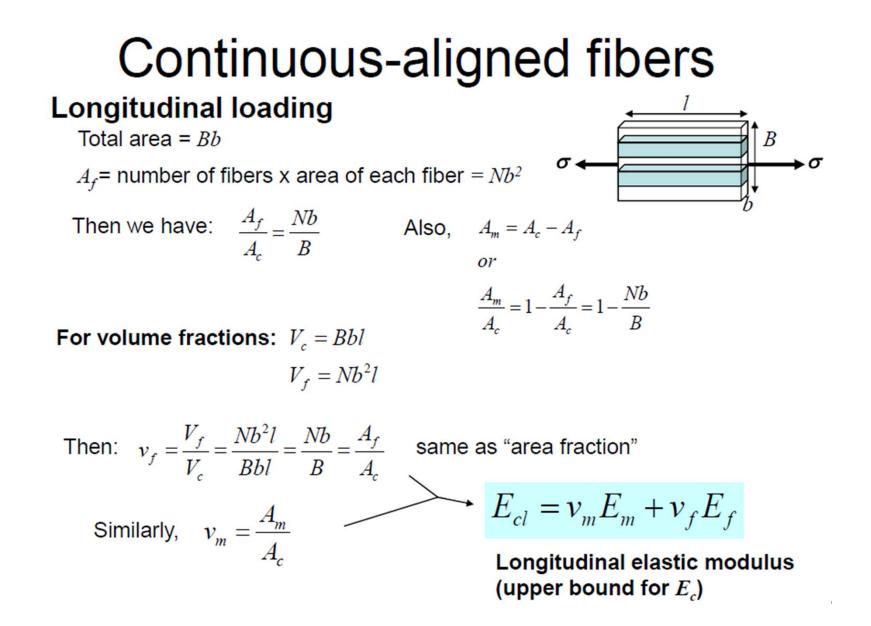


When $l >> l_c$ (typically $l > 15 l_c$), we can simplify to:



Isostrain Conditions





Continuous-aligned fibers

Longitudinal loading

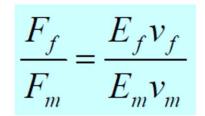
What about the load on the matrix and the fibers?

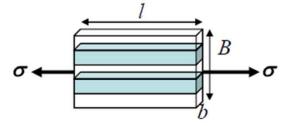
$$\frac{F_f}{F_m} = ? \qquad \qquad F = \sigma A$$

$$\frac{F_f}{F_m} = \frac{\sigma_f A_f}{\sigma_m A_m} = \frac{\sigma_f v_f}{\sigma_m v_m}$$

With $\sigma = E\varepsilon$

 $\frac{F_f}{F_m} = \frac{E_f \varepsilon_f v_f}{E_m \varepsilon_m v_m} \quad \xrightarrow{\text{Isostrain conditions}}$

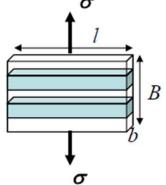




Continuous-aligned fibers Transverse loading

Stress, rather than strain, is the same in this case:

 $\sigma_c = \sigma_f = \sigma_m$ ISOSTRESS condition



The total elongation will be the sum of elongation of the components: $\Delta L_c = \Delta L_f + \Delta L_m$

Strain = $\varepsilon_c = \frac{\Delta L_c}{L_c} = \frac{\Delta L_f}{L_c} + \frac{\Delta L_m}{L_c}$ Where L_c = length of the composite along the direction of stress = B

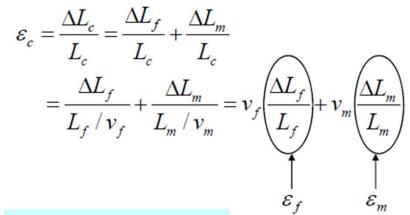
Again, to express in terms of volume fractions:

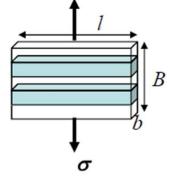
$$L_{f} = Nb$$

$$\frac{L_{f}}{L_{c}} = \frac{Nb}{B} = v_{f}$$
Rearrange $L_{c} = \frac{L_{f}}{v_{f}}$
Similarly, $L_{c} = \frac{L_{m}}{v_{m}}$

Continuous-aligned fibers

Transverse loading





$$\mathcal{E}_{c} = v_{m}\mathcal{E}_{m} + v_{f}\mathcal{E}_{f}$$

From stress-strain relation; $\mathcal{E} = \frac{\sigma}{F}$

Lower bound for E_c (transverse modulus)

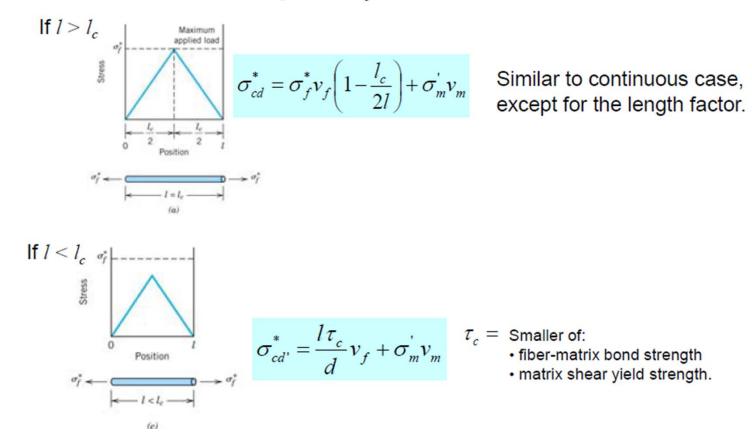
$$\frac{\sigma_c}{E_c} = v_m \frac{\sigma_m}{E_m} + v_f \frac{\sigma_f}{E_f}$$

$$E_{ct} = \frac{E_m E_f}{v_m E_f + v_f E_m}$$

Applying isostress condition and rearranging gives

Discontinuous & aligned fibers

Discontinuous when fiber length < 15 l_c



Discontinuous & random fibers

Discontinuous, random 2D fibers

- Example: Carbon-Carbon

 -process: fiber/pitch, then
 burn out at up to 2500C.
 - --uses: disk brakes, gas turbine exhaust flaps, nose cones.

$$E_c = E_m V_m + KE_f V_f$$

efficiency factor

(depends on v_f and E_f/E_m):

- --aligned 1D: K = 1 (anisotropic)
- --random 2D: K = 3/8 (2D isotropy)

--random 3D: K = 1/5 (3D isotropy)

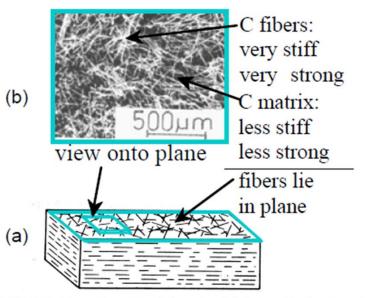


Table 16.2 Properties of Unreinforced and Reinforced Polycarbonates with Randomly Oriented Glass Fibers

Property	Unreinforced	Fiber Reinforcement (vol%)		
		20	30	40
Specific gravity	1.19-1.22	1.35	1.43	1.52
Tensile strength [MPa (ksi)]	59-62 (8.5-9.0)	110 (16)	131 (19)	159 (23)
Modulus of elasticity [GPa (10 ⁶ psi)]	2.24-2.345 (0.325-0.340)	5.93 (0.86)	8.62 (1.25)	11.6 (1.68)
Elongation (%)	90-115	4-6	3-5	3-5
Impact strength, notched Izod (lb _f /in.)	12-16	2.0	2.0	2.5

Source: Adapted from Materials Engineering's Materials Selector, copyright @ Penton/IPC.